

1,3-Diphenylpropane-1,3-diamines, IV¹⁾

Synthesis of 1,3-Bis(hydroxy-halogenophenyl)propane-1,3-diamines and their Pt(II) Complexes

Part B: Preparation of the Pt(II) Complexes^{*)}Thomas Kammermeier and Wolfgang Wiegreb^{*)}*

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1,3-Diphenylpropan-1,3-diamine, 4. Mitt.¹⁾:

Synthese von 1,3-Bis(hydroxy-halogenphenyl)propan-1,3-diaminen und ihren Pt(II) Komplexen

Teil B: Herstellung der Pt(II) Komplexe^{*)}

The preparation of the Pt(II) complexes of the diamines described in Part A with Cl⁻, I⁻, SO₄²⁻, and water as additional ligands is reported.

Über die Herstellung der Pt(II) Komplexe der in Teil A beschriebenen Diamine mit Cl⁻, I⁻, SO₄²⁻ und Wasser als zusätzlichen Liganden wird berichtet.

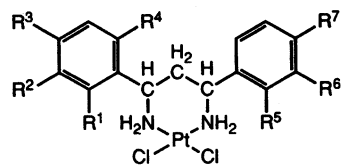
Dichloro-platinum(II) complexes

The title complexes were prepared as described for the 1,2-diphenylethane-1,2-diamino-Pt(II) complexes²⁾. In brief, K₂PtCl₄ in water was added drop by drop to the dihydrochlorides of the ligands, dissolved in water or (lipophilic ligands) in water/tert. butanol at 40°C and pH 6.0-6.5. This range is important and was maintained by adding 0.1 N NaOH within small intervals. If the reaction mixture becomes too acidic the pertinent 1,3-diammoniumpropane-tetrachloro-Pt(II) derivative may come up. Basic conditions lead to exchange of Cl⁻ against OH⁻. Moreover Pt⁰ may be formed by reduction²⁾³⁾. Analogously to the 1,2-diphenylethane-1,2-diamines the formation of the *meso*- and *erythro*-stereomeric Pt complexes need longer reaction times and the yields are lower in comparison with the *rac*- and *threo*-complexes which were obtained as analytically pure solids in most cases. - On account of their sensitivity to oxygen, the ligands **92** and **93** (Part A) with a catechol increment could not be obtained as bases. Therefore, their chloride-complexes could not be prepared directly.

As mentioned above, the *o*-methoxy-substituted ligands **60** and **61** (Part A) could not be converted to the corresponding phenols. Therefore, these ethers were reacted to the pertinent Pt(II) complexes directly. - The complexes **114-139** so obtained are shown in Table 1.

Although diaqua/sulfato-Pt(II) complexes can be prepared from the pertinent dichloro complexes - probably as a mix-

Tab. 1: Dichloro-platinum(II) complexes 114-139



comp.	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷
114, 115	OCH ₃	H	H	H	OCH ₃	H	H
116, 117	H	OH	H	H	H	OH	H
118, 119	H	H	OH	H	H	H	OH
120, 121	H	H	OH	H	F	H	OH
122, 123	H	H	OH	H	Cl	H	OH
124, 125	H	H	OH	H	Br	H	OH
126, 127	Cl	H	OH	Cl	OH	H	H
128, 129	Cl	H	OH	Cl	H	OH	H
130, 131	Cl	H	OH	Cl	H	H	OH
132, 133	F	H	OH	H	F	H	OH
134, 135	Cl	H	OH	H	Cl	H	OH
136, 137	Cl	H	OH	Cl	F	H	OH
138, 139	Cl	H	OH	Cl	Cl	H	OH

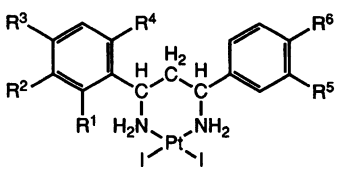
ture with coordinated and counterionic sulfate ligands (this we want to indicate by our formulation "diaqua/sulfato", cf. the IR-spectra of the complexes as discussed in forthcoming Part V)-, the formation *via* the diiodo complexes is favourable: I⁻ has a stronger *trans*-effect than Cl⁻⁴⁾. Therefore, the bond between Pt and the ligand arranged *trans* to I⁻ is weakened, resulting in a kinetically favoured substitution. Moreover, *meso*- and *erythro*-diastereomers precipitate as analytically pure *diiodo* complexes. Generally, the dihydrochlorides of the ligands were treated with K₂PtCl₄ afford-

^{*)} Part A: preceeding paper. - As parts A and B are closely correlated to each other, the compounds are numbered consecutively.

⁺⁾ Dedicated to Prof. Dr. S. Ebel, Würzburg, on the occasion of his 60th birthday.

ing complexes **140-151**. In case of the catechol derivatives **92** and **93** (Part A) the dihydrobromides - resulting from BBr_3 -induced ether cleavage - were used, needing longer reaction times than the dihydrochlorides as expected.

Tab. 2: Diiodo-platinum(II) complexes **140-151**

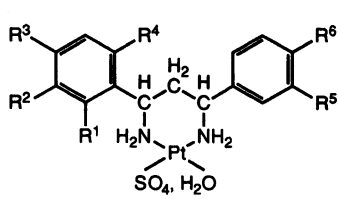


comp.	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
140, 141	H	OH	H	H	OH	H
142, 143	F	H	OH	H	H	OH
144, 145	Cl	H	OH	H	H	OH
146, 147	Cl	H	OH	Cl	OH	H
148, 149	Cl	H	OH	Cl	H	OH
150, 151	H	OH	OH	H	OH	OH

Diaqua/sulfato-platinum(II) complexes

These complexes were obtained from the diiodo-complexes by treatment with Ag_2SO_4 /water in the dark, using a slight excess of the diiodo-complexes. The diaqua/sulfato-complexes are soluble in water and were obtained by freeze-drying. Again the bis-catechol complex **150** did not react properly. Special features of the NMR spectra of the ligands and the complexes cited here, establishing their stereochemistry, will be discussed with reference to Fig. 1 (Part III, preceding paper) in Part V of this series.

Tab. 3: Diaqua/sulfato-platinum(II) complexes **152-162**



comp.	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
152, 153	H	OH	H	H	OH	H
154	H	OH	OH	H	OH	OH
155, 156	F	H	OH	H	H	OH
157, 158	Cl	H	OH	H	H	OH
159, 160	Cl	H	OH	Cl	OH	H
161, 162	Cl	H	OH	Cl	H	OH

*) For the sake of clearness only the ions for ^{35}Cl are cited in the mass spectra of Cl-containing compounds.

Experimental Part

General remarks: see preceding paper

Dichloro-Pt(II) complexes

The pertinent 1,3-diphenylpropane-1,3-diamines were liberated from 0.5 mmoles of their dihydrobromides (if not otherwise stated) by cc on silica with the solvents I or II as indicated. The solvent was removed *in vacuo* at 40°, the base was dried at the oil pump, suspended in 10 ml of water and dissolved by 1 ml of 2N HCl. After filtration this solution was warmed to 40° and the pH value was adjusted to 6.0-6.5 by 0.1N NaOH. In the cases of more lipophilic bases the solutions became turbid, and 10 ml of tert-butanol were added in order to improve solubility. Then 208 mg K_2PtCl_4 (0.5 mmoles) (Janssen) in 5 ml of water were added drop by drop with stirring. Stirring was continued for 12-14 h under light protection, whilst pH 6.5 was adjusted every 30-45 min by addition of 0.1N NaOH. After this time the pH-value did not change in most cases, so that the precipitated complex can be collected by suction filtration, washing with 2N HCl and water and drying at the oil pump for several days over P_4O_{10} at 100°. In some cases the complexes had to be purified by dissolving in a very small quantity of DMF and precipitation with 5% NaCl solution.- Solvent I: MeOH/conc. ammonia 100/1.5 (v/v).- Solvent II: EtOH 96%/conc. ammonia 100/1.5 (v/v).- The light-grey, non-crystalline complexes melt with decomposition.

meso-Dichloro-1,3-bis-(2-methoxyphenyl)propane-1,3-diamino-Pt(II) (**114***)

From **60** x 2 HCl; solvent I; 25%, m.p. 205-208°.- $\text{C}_{17}\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_2\text{Pt}$ (552.4) Calcd. C 37.0 H 4.01 N 5.1 Found C 37.4 H 4.09 N 4.8.- FT-IR (KBr): $\tilde{\nu}$ = 3258 s, 3189, 3120 m (NH_2); 2957 m, 2927 m (C-H aliph.); 2857 m (OCH_3); 1603 s, 1595 s (C=C and NH_2).- $^1\text{H-NMR}$ ($[\text{D}_7]\text{DMF}$): δ (ppm/250 MHz) = 7.52-6.82 (m; 8H arom.), 5.53-5.09 (m; 4H, NH_2 ; H/D-exch.), 4.70-4.47 (m; 2H, CH; H/D-exch.: 4.59; ABX_2 , $^3J_{\text{AX}} = 1.0$ Hz, $^3J_{\text{BX}} = 1.04$ Hz), 3.93 (s; 6H, OCH_3), 2.64-2.57 (ABX_2 ; $^2J_{\text{AB}} = 14.0$ Hz, $^3J_{\text{BX}} = 10.4$ Hz, 1H, CH_2 , H_{ax}), 2.30-2.13 (ABX_2 ; $^2J_{\text{AB}} = 14.0$ Hz, $^3J_{\text{AX}} = 1.0$ Hz, 1H, CH_2 , H_{eq}).- PI-FAB-MS (glycerol/DMSO/ ^{194}Pt): m/z = 1065.1 ($(\text{L}_2\text{Pt}_2\text{Cl}_3)^+$); 629.2 ((M + H + DMSO) $^+$); 593.3 ((M - Cl + DMSO) $^+$); 515.3 ((M - Cl) $^+$).

Dimers of the type $[(\text{L}_2\text{Pt}_2\text{Cl}_3)^+]$ were also observed by *Sperl*⁵⁾ in the PI-FAB-spectra of *cis*-dichloro-Pt(II) complexes of estradiol derivatives.

rac-Dichloro-1,3-bis-(2-methoxyphenyl)propane-1,3-diamino-Pt(II) (**115**)

From **61** x 2 HCl; solvent I; 11%, m.p. 209-211°.- $\text{C}_{17}\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_2\text{Pt}$ (552.4) Calcd. C 37.0 H 4.01 N 5.1 Found C 36.4 H 3.94 N 5.0.- FT-IR (KBr): $\tilde{\nu}$ = 3264 s, 3191 m, 3114 m (NH_2); 3017 w (C-H arom.); 2969 m, 2938 m (C-H aliph.); 2840 m (OCH_3); 1601 s, 1589 s (C=C and NH_2).- $^1\text{H-NMR}$ ($[\text{D}_7]\text{DMF}$): δ (ppm/250 MHz) = 8.47-6.91 (m; 8H arom.), 5.66-5.50 (m; 2H, NH_2 ; H/D-exch.), 5.39-5.10 (m; 2H, NH_2 ; H/D-exch.), 4.38-4.17 (m; 2H, CH; H/D-exch.: 4.27; A_2X_2 , $^3J_{\text{AX}} = 5.1$ Hz), 3.77 (s; 6H, OCH_3), 2.38 (A_2X_2 , $^3J_{\text{AX}} = 5.1$ Hz, 2H, CH_2).- PI-FAB-MS (glycerol/DMSO/ ^{194}Pt): m/z = 1064.9 ($(\text{L}_2\text{Pt}_2\text{Cl}_3)^+$); 643.1 ((M + H + glycerol) $^+$); 629.1 ((M + H + DMSO) $^+$); 593.2 ((M - Cl + DMSO) $^+$); 551.2 ((M + H) $^+$); 515.2 ((M - Cl) $^+$).

meso-Dichloro-1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**116**)

From **88**; solvent I; 45%, m.p. 227-230°.- $\text{C}_{15}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2\text{Pt}$ (524.3) Calcd. C 34.4 H 3.46 N 5.3 Found C 34.4 H 3.32 N 5.3.- FT-IR (KBr): $\tilde{\nu}$ = 3392 s, br (OH); 3266 s, 3201 s, 3185 s, 3133 s (NH_2); 2956 w, 2930 w (C-H aliph.); 1593 s (C=C and NH_2).- CW-IR (KBr): $\tilde{\nu}$ = 330 sh, 320 m

(Pt-Cl).- $^1\text{H-NMR}$ ($[\text{D}_7]\text{DMF}$): δ (ppm/250 MHz) = 9.67 (s, br; 2H, OH; H/D-exch.), 7.21-6.69 (m; 8H arom.,), 5.72-5.49 (m, br; 2H, NH_2 ; H/D-exch.), 5.28-5.07 (m, br; 2H, NH_2 ; H/D-exch.), 4.53-4.36 (m; 2H, CH; H/D-exch.): 4.43; ABX_2 , $^3J_{\text{AX}} = 1.0$ Hz, $^3J_{\text{BX}} = 11.9$ Hz), 2.44 (ABX_2 ; $^2J_{\text{AB}} = 14.8$ Hz, $^3J_{\text{BX}} = 11.9$ Hz, 1H, CH_2 , H_{ax}), 1.98 (ABX_2 ; $^2J_{\text{AB}} = 14.8$ Hz, $^3J_{\text{AX}} = 1.0$ Hz, 1H, CH_2 , H_{eq}).- $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm/50 MHz) = 158.7 (C'-4 arom.), 144.6 (C'-1 arom.), 130.2 (C-H arom.), 117.8 (C-H arom.), 115.5 (C-H arom.), 114.4 (C-H arom.), 60.0 (CH), 43.3 (CH_2).- PI-FAB-MS (glycerol/DMSO/ ^{194}Pt): $m/z = 1009.0$ ($(\text{L}_2\text{Pt}_2\text{Cl}_3)^+$); 615.2 ((M + H + glycerol) $^+$); 601.1 ((M + H + DMSO) $^+$); 579.2 ((M - Cl + glycerol) $^+$); 565.2 ((M - Cl + DMSO) $^+$); 523.2 ((M + H) $^+$); 487.2 ((M - Cl) $^+$).

rac-Dichloro-1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino Pt(II) (117)

From **89**; solvent I; 54%, m.p. 225-229°. - $\text{C}_{15}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2\text{Pt} \times \text{H}_2\text{O}$ (542.3) Calcd. C 33.2 H 3.72 N 5.2 Found C 33.2 H 3.44 N 5.2.- FT-IR (KBr): $\tilde{\nu} = 3424$ s, br (OH); 3253 s, 3193 s, 3110 s (NH_2); 2961 w, 2934 w (C-H aliph.); 1611 m, 1589 s (C=C and NH_2).- CW-IR (KBr): $\tilde{\nu} = 320$ m (Pt-Cl).- $^1\text{H-NMR}$ ($[\text{D}_7]\text{DMF}$): δ (ppm/250 MHz) = 9.75 (s; 2H, OH; H/D-exch.), 7.27-7.21 (m; 6H arom.), 6.83-6.78 (m; 2H arom.), 5.66-5.47 (m; 2H, NH_2 ; H/D-exch.), 5.47-5.19 (m; 2H, NH_2 ; H/D-exch.), 3.94 (s, br; 2H, CH; H/D-exch.): 3.97; A_2X_2 , $^3J_{\text{AX}} = 5.0$ Hz), 2.41 (A_2X_2 ; $^3J_{\text{AX}} = 5.0$ Hz, 2H, CH_2).- $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm/50 MHz) = 158.7 (C'-4 arom.), 143.1 (C'-1 arom.), 130.0 (C-H arom.), 117.7 (C-H arom.), 115.2 (C-H arom.), 114.1 (C-H arom.), 53.9 (CH), 41.9 (CH_2).- PI-FAB-MS (glycerol/DMSO/ ^{194}Pt): $m/z = 1008.9$ ($(\text{L}_2\text{Pt}_2\text{Cl}_3)^+$); 707.1 ((M + H + 2 glycerol) $^+$); 615.2 ((M + H + glycerol) $^+$); 601.1 ((M + H + DMSO) $^+$); 579.1 ((M - Cl + glycerol) $^+$); 565.1 ((M - Cl + DMSO) $^+$); 523.1 ((M + H) $^+$); 487.2 ((M - Cl) $^+$).

meso-Dichloro-1,3-bis-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (118)

From **90**; solvent I; 33%, m.p. 216-219°. - $\text{C}_{15}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2\text{Pt}$ (524.3) Calcd. C 34.4 H 3.46 N 5.3 Found C 34.6 H 3.85 N 4.9.- FT-IR (KBr): $\tilde{\nu} = 3482$ s, br (OH); 3249 s, 3237 s, 3204 s, 3121 s (NH_2); 3023 w (C-H arom.); 2957 w, 2919 w (C-H aliph.); 1613 s, 1597 s (C=C and NH_2).- $^1\text{H-NMR}$ ($[\text{D}_7]\text{DMF}$): δ (ppm/250 MHz) = 9.64 (s; 2H, OH; H/D-exch.), 7.40, 6.81 (AA'BB'; $^3J = 8.5$ Hz, 8H arom.), 5.67-5.40 (m; 2H, NH_2 ; H/D-exch.), 5.13-4.92 (m; 2H, NH_2 ; H/D-exch.), 4.51-4.33 (m; 2H, CH; H/D-exch.): 4.39; ABX_2 , $^3J_{\text{AX}} = 1.0$ Hz, $^3J_{\text{BX}} = 11.3$ Hz), 2.52 (ABX_2 ; $^2J_{\text{AB}} = 15.3$ Hz, $^3J_{\text{BX}} = 11.3$ Hz, 1H, CH_2 , H_{ax}), 1.93 (ABX_2 ; $^2J_{\text{AB}} = 15.3$ Hz, $^3J_{\text{AX}} = 1.0$ Hz, 1H, CH_2 , H_{eq}).- PI-FAB-MS (glycerol/DMSO/ ^{194}Pt): $m/z = 1009.2$ ($(\text{L}_2\text{Pt}_2\text{Cl}_3)^+$); 707.4 ((M + H + 2 glycerol) $^+$); 615.2 ((M + H + glycerol) $^+$); 601.2 ((M + H + DMSO) $^+$); 579.3 ((M - Cl + glycerol) $^+$); 565.3 ((M - Cl + DMSO) $^+$); 487.3 ((M - Cl) $^+$).

rac-Dichloro-1,3-bis-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (119)

From **91**; solvent I; 48%, m.p. 207-210°. - $\text{C}_{15}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2\text{Pt}$ (524.3) Calcd. C 34.4 H 3.46 N 5.3 Found C 34.4 H 3.62 N 5.3.- FT-IR (KBr): $\tilde{\nu} = 3436$ s, br (OH); 3264 s, 3251 s, 3199 s, 3114 s, 3114 s (NH_2); 3021 w (C-H arom.); 2961 w, 2929 w (C-H aliph.); 1613 s, 1595 s (C=C and NH_2).- $^1\text{H-NMR}$ ($[\text{D}_7]\text{DMF}$): δ (ppm/250 MHz) = 9.66 (s; 2H, OH; H/D-exch.), 7.63, 6.86 (AA'BB'; $^3J = 8.6$ Hz, 8H arom.), 5.63-5.10 (m, br; 4H, NH_2 ; H/D-exch.), 3.96 (s, br; 2H, CH; H/D-exch.): 3.99; A_2X_2 , $^3J_{\text{AX}} = 4.9$ Hz), 2.38 (A_2X_2 ; $^3J_{\text{AX}} = 4.9$ Hz, 2H, CH_2).- PI-FAB-MS (glycerol/DMSO/ ^{194}Pt): $m/z = 615.2$ ((M + H + glycerol) $^+$); 601.2 ((M + H + DMSO) $^+$); 579.2 ((M - Cl + glycerol) $^+$); 565.2 ((M - Cl + DMSO) $^+$); 487.2 ((M - Cl) $^+$).

erythro-Dichloro-1-(2-fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (120)

From **94**; solvent I; 43%, m.p. 215-219°. - $\text{C}_{15}\text{H}_{17}\text{Cl}_2\text{FN}_2\text{O}_2\text{Pt}$ (542.3) Calcd. C 33.2 H 3.16 N 5.2 Found C 33.8 H 3.39 N 5.0.- FT-IR (KBr): $\tilde{\nu} =$

3407 s, br (OH); 3239 s, 3201 s, 3125 s (NH_2); 2957 w, 2927 w (C-H aliph.); 1628 s (NH_2); 1597 s (C=C).- CW-IR (KBr): $\tilde{\nu} = 320$ m (Pt-Cl).- $^1\text{H-NMR}$ ($[\text{D}_7]\text{DMF}$): δ (ppm/250 MHz) = 10.18 (s; 1H, OH; H/D-exch.), 9.66 (s; 1H, OH; H/D-exch.), 7.49 (t; $^3J = 8.5$ Hz, $^4J_{\text{HF}} = 8.5$ Hz, 1H arom.), 7.41, 6.82 (AA'BB'; $^3J_{\text{AB}} = 8.5$ Hz, 4H arom.), 6.72-6.56 (m; 2H arom.), 5.60-5.49 (m; 1H, NH_2 ; H/D-exch.), 5.47-5.79 (m; 1H, NH_2 ; H/D-exch.), 5.34-5.21 (m; 1H, NH_2 ; H/D-exch.), 5.02-4.92 (m; 1H, NH_2 ; H/D-exch.), 4.67-4.51 (m; 1H, CH; H/D-exch.): 4.57; ABXY , $^3J_{\text{AX}} = ^3J_{\text{AY}} = 1.5$ Hz, $^3J_{\text{BX}} = ^3J_{\text{BY}} = 10.7$ Hz), 4.51-4.35 (m; 1H, CH; partial overlap with solvent signals after H/D-exch.), 2.54 (ABXY ; $^2J_{\text{AB}} = 14.2$ Hz, $^3J_{\text{BX}} = ^3J_{\text{BY}} = 10.7$ Hz, 1H, CH_2 , H_{ax}), 1.99 (ABXY ; $^2J_{\text{AB}} = 14.2$ Hz, $^3J_{\text{AX}} = ^3J_{\text{AY}} = 1.5$ Hz, 1H, CH_2 , H_{eq}).- PI-FAB-MS (glycerol/DMSO/ ^{194}Pt): $m/z = 633.4$ ((M + H + glycerol) $^+$); 619.3 ((M + H + DMSO) $^+$); 597.4 ((M - Cl + glycerol) $^+$); 583.3 ((M - Cl + DMSO) $^+$); 505.4 ((M - Cl) $^+$).

threo-Dichloro-1-(2-fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (121)

From **95**, solvent I; 55%, m.p. 221-224°. - $\text{C}_{15}\text{H}_{17}\text{Cl}_2\text{FN}_2\text{O}_2\text{Pt}$ (542.3) Calcd. C 33.2 H 3.16 N 5.2 Found C 33.4 H 3.22 N 5.1.- FT-IR (KBr): $\tilde{\nu} = 3432$ s, br (OH); 3264 s, 3251 s, 3197 s, 3120 s (NH_2); 3023 w (C-H arom.); 2967 w, 2923 w (C-H aliph.); 1624 s (NH_2); 1593 s (C=C).- CW-IR (KBr): $\tilde{\nu} = 330$ m, 320 m (Pt-Cl).- $^1\text{H-NMR}$ ($[\text{D}_7]\text{DMF}$): δ (ppm/250 MHz) = 9.95 (s, br; 2H, OH; H/D-exch.), 8.30 (t; $^3J = 8.9$ Hz, $^4J_{\text{HF}} = 8.9$ Hz, 1H arom.), 7.71, 6.87 (AA'BB'; $^3J_{\text{AB}} = 8.5$ Hz, 4H arom.), 6.80-6.55 (m; 2H arom.), 5.70-5.45 (m; 2H, NH_2 ; H/D-exch.), 5.45-5.19 (m; 2H, NH_2 ; H/D-exch.), 4.20 (s, br; 1H, CH; H/D-exch.): 4.18; A_2XY , $^3J_{\text{AX}} = ^3J_{\text{AY}} = 5.0$ Hz), 4.03 (s, br; 1H, CH; H/D-exch.): 4.08; A_2XY , $^3J_{\text{AX}} = ^3J_{\text{AY}} = 5.0$ Hz), 2.35 (A_2XY ; $^3J_{\text{AX}} = ^3J_{\text{AY}} = 5.0$ Hz, 2H, CH_2).- PI-FAB-MS (glycerol/DMSO/ ^{194}Pt): $m/z = 1045.3$ ($(\text{L}_2\text{Pt}_2\text{Cl}_3)^+$); 725.5 ((M + H + 2 glycerol) $^+$); 633.4 ((M + H + glycerol) $^+$); 619.1 ((M + H + DMSO) $^+$); 597.4 ((M - Cl + glycerol) $^+$); 583.3 ((M - Cl + DMSO) $^+$); 541.3 ((M + H) $^+$); 505.4 ((M - Cl) $^+$).

erythro-Dichloro-1-(2-chloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (122)

From **96**; solvent I; 25%, m.p. 207-210°. - $\text{C}_{15}\text{H}_{17}\text{Cl}_3\text{N}_2\text{O}_2\text{Pt} \times 1.5 \text{ H}_2\text{O}$ (585.8) Calcd. C 30.8 H 3.44 N 4.8 Found C 30.8 H 3.22 N 4.7.- FT-IR (KBr): $\tilde{\nu} = 3397$ s, br (OH); 3262 s, 3199 s, 3116 s (NH_2); 2979 w, 2957 w, 2925 w (C-H aliph.); 1611 s, 1586 s (C=C and NH_2).- $^1\text{H-NMR}$ ($[\text{D}_7]\text{DMF}$): δ (ppm/250 MHz) = 9.87 (s, br; 2H, OH; H/D-exch.), 7.58 (d; $^3J = 8.6$ Hz, 1H arom.), 7.42, 6.83 (AA'BB'; $^3J_{\text{AB}} = 8.5$ Hz, 4H arom.), 6.92-6.81 (m; 2H arom.), 5.58-5.42 (m; 2H, NH_2 ; H/D-exch.), 5.30-5.20 (m; 1H, NH_2 ; H/D-exch.), 5.07-4.96 (m; 1H, NH_2 ; H/D-exch.), 4.70-4.55 (m; 1H, CH; H/D-exch.): 4.61; ABXY , $^3J_{\text{AX}} = ^3J_{\text{AY}} = 1.5$ Hz, $^3J_{\text{BX}} = ^3J_{\text{BY}} = 11.2$ Hz), 4.48-4.33 (m; 1H, CH; H/D-exch.): 4.34; ABXY , $^3J_{\text{AX}} = ^3J_{\text{AY}} = 1.5$ Hz, $^3J_{\text{BX}} = ^3J_{\text{BY}} = 11.2$ Hz), 2.50 (ABXY ; $^2J_{\text{AB}} = 15.0$ Hz, $^3J_{\text{BX}} = ^3J_{\text{BY}} = 11.2$ Hz, 1H, CH_2 , H_{ax}), 1.95 (ABXY ; $^2J_{\text{AB}} = 15.0$ Hz, $^3J_{\text{AX}} = ^3J_{\text{AY}} = 1.5$ Hz, 1H, CH_2 , H_{eq}).- PI-FAB-MS (glycerol/DMSO/ ^{194}Pt): $m/z = 1076.9$ ($(\text{L}_2\text{Pt}_2\text{Cl}_3)^+$); 649.2 ((M + H + glycerol) $^+$); 635.2 ((M + H + DMSO) $^+$); 613.2 ((M - Cl + glycerol) $^+$); 599.3 ((M - Cl + DMSO) $^+$); 521.2 ((M - Cl) $^+$).

threo-Dichloro-1-(2-chloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (123)

From **97**; solvent I; 24%, m.p. 221-225°. - $\text{C}_{15}\text{H}_{17}\text{Cl}_3\text{N}_2\text{O}_2\text{Pt}$ (558.8) Calcd. C 32.2 H 3.07 N 5.0 Found C 32.4 H 2.90 N 4.9.- FT-IR (KBr): $\tilde{\nu} = 3397$ s, br (OH); 3251 s, 3201 s, 3125 s (NH_2); 2963 w, 2929 w (C-H aliph.); 1613 s, 1593 s (C=C and NH_2).- $^1\text{H-NMR}$ ($[\text{D}_7]\text{DMF}$): δ (ppm/250 MHz) = 10.21 (s, br; 1H, OH; H/D-exch.), 9.67 (s, br; 1H, OH; H/D-exch.), 8.38 (d; $^3J = 8.5$ Hz, 1H arom.), 7.81 (d, part of an AA'BB' system; $^3J_{\text{AB}} = 8.4$ Hz, 2H arom.), 6.95-6.82 (m; 4H arom.), 5.72-5.58

(m, br; 1H, NH₂; H/D-exch.), 5.55-5.40 (m, br; 2H, NH₂; H/D-exch.), 5.37-5.24 (m, br; 1H, NH₂; H/D-exch.), 4.28 (s, br; 1H, CH; H/D-exch.: 4.27; A₂XY, ³J_{AX} = ³J_{AY} = 5.0 Hz), 4.07 (s, br; 1H, CH; partial overlap with solvent signals after H/D-exch.), 2.33 (A₂XY; ³J_{AX} = ³J_{AY} = 5.0 Hz, 2H, CH₂)- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1076.9 ((L₂Pt₂Cl₃)⁺); 649.0 ((M + H + glycerol)⁺); 635.0 ((M + H + DMSO)⁺); 613.1 ((M - Cl + glycerol)⁺); 599.1 ((M - Cl + DMSO)⁺); 521.1 ((M - Cl)⁺).

erythro-Dichloro-1-(2-bromo-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**124**)

From **98**; solvent I; 16%, m.p. 198-202°.- C₁₅H₁₇BrCl₂N₂O₂Pt x H₂O (621.2) Calcd. C 29.0 H 3.08 N 4.5 Found C 28.8 H 2.86 N 4.4.- FT-IR (KBr): $\tilde{\nu}$ = 3378 s, br (OH); 3260 s, 3120 s (NH₂); 2963 w (C-H aliph.); 1609 s, 1589 m, 1570 m (C=C and NH₂)- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.11 (s, br; 1H, OH; H/D-exch.), 9.89 (s, br; 1H, OH; H/D-exch.), 7.60 (d; ³J = 8.4 Hz, 1H arom.), 7.42, 6.83 (AA'BB'; ³J_{AB} = 8.2 Hz, 4H arom.), 7.18-6.77 (m; 2H arom.), 5.62-5.45 (m; 2H, NH₂; H/D-exch.), 5.22-5.09 (m; 1H, NH₂; H/D-exch.), 5.00-4.86 (m; 1H, NH₂; H/D-exch.), 4.70-4.51 (m; 1H, CH; H/D-exch.: 4.59; ABXY, ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 10.5 Hz), 4.48-4.29 (m; 1H, CH; H/D-exch.: 4.34; ABXY, ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 10.5 Hz), 2.48 (ABXY; ²J_{AB} = 14.5 Hz, ³J_{BX} = ³J_{BY} = 10.5 Hz, 1H, CH₂, H_{ax}), 2.00 (ABXY; ²J_{AB} = 14.5 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq})- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 693.0 ((M + H + glycerol)⁺); 643.0 ((M - Cl + DMSO)⁺).

threo-Dichloro-1-(2-bromo-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**125**)

From **99**; solvent I, 15%, m.p. 211-215°.- C₁₅H₁₇BrCl₂N₂O₂Pt x 2 H₂O (639.2) Calcd. C 28.2 H 3.31 N 4.4 Found C 28.2 H 3.36 N 4.4.- FT-IR (KBr): $\tilde{\nu}$ = 3394 s, br (OH); 3247 s, 3201 s, 3123 s (NH₂); 2959 w, 2929 w (C-H aliph.); 1609 s, 1593 s (C=C and NH₂)- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.16 (s, br; 1H, OH; H/D-exch.), 9.67 (s, br; 1H, OH; H/D-exch.), 8.37 (d; ³J = 8.5 Hz, 1H arom.), 7.83, 6.87 (AA'BB'; ³J_{AB} = 8.5 Hz, 4H arom.), 7.05-6.93 (m; 2H arom.), 5.72-5.58 (m, br; 1H, NH₂; H/D-exch.), 5.55-5.40 (m, br; 2H, NH₂; H/D-exch.), 5.37-5.24 (m, br; 1H, NH₂; H/D-exch.), 4.28 (s, br; 1H, CH; partial overlap by solvent signals after H/D-exch.), 4.07 (s, br; 1H, CH; partial overlap with solvent signals after H/D-exch.), 2.32 (A₂XY; ³J_{AX} = ³J_{AY} = 5.0 Hz, 2H, CH₂)- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1165.7 ((L₂Pt₂Cl₃)⁺); 693.2 ((M + H + glycerol)⁺); 658.2 ((M - Cl + glycerol)⁺); 643.2 ((M - Cl + DMSO)⁺), 565.1 ((M - Cl)⁺).

erythro-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(2-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**126**)

From **100**; solvent II; 50%, m.p. 194-196°.- C₁₅H₁₆Cl₄N₂O₂Pt x H₂O (611.2) Calcd. C 29.5 H 2.97 N 4.6 Found C 29.6 H 3.07 N 4.5.- FT-IR (KBr): $\tilde{\nu}$ = 3407 s, br (OH); 3272 s, 3228 s (NH₂); 2968 w, 2925 w (C-H aliph.); 1605 s, 1570 s (C=C and NH₂)- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.52-6.82 (m; 4H arom.), 6.94 (s; 2H arom.), 6.13-6.00 (m; 1H, NH₂; H/D-exch.), 5.68-5.44 (m; 1H, NH₂; H/D-exch.), 5.44-5.22 (m; 1H, NH₂; H/D-exch.), 5.19-5.01 (m; 1H, CH; H/D-exch.: 5.08; ABXY, ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 10.4 Hz), 5.01-4.81 (m; 1H, NH₂; H/D-exch.), 4.67-4.47 (m; 1H, CH; H/D-exch.: 4.53; ABXY, ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 10.4 Hz), 3.16 (ABXY; ²J_{AB} = 15.3 Hz, ³J_{BX} = ³J_{BY} = 10.4 Hz, 1H, CH₂, H_{ax}, partial overlap by solvent signals), 2.01 (ABXY; ²J_{AB} = 15.3 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq})- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1145.3 ((L₂Pt₂Cl₃)⁺); 775.2 ((M + H + 2 glycerol)⁺), 683.2 ((M + H + glycerol)⁺); 669.2 ((M + H + DMSO)⁺); 647.2 ((M - Cl + glycerol)⁺); 633.2 ((M - Cl + DMSO)⁺); 591.3 ((M + H)⁺); 555.3 ((M - Cl)⁺).

threo-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(2-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**127**)

From **101**; solvent II; 35%, m.p. 196-198°.- C₁₅H₁₆Cl₄N₂O₂Pt x tert.-C₄H₁₀O (667.3) Calcd. C 34.2 H 3.93 N 4.2 Found C 34.5 H 3.76 N 4.5.- FT-IR (KBr): $\tilde{\nu}$ = 3384 s, br (OH); 3255 s, 3208 m, 3185 m, 3116 s (NH₂); 2971 w, 2936 w (C-H aliph.); 1605 s, 1574 s (C=C and NH₂)- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.68 (s, br; 1H, OH; H/D-exch.), 10.06 (s, br; 1H, OH; H/D-exch.), 9.17 (d; ³J = 7.6 Hz, 1H arom.), 7.22-6.94 (m; 3H arom.), 6.85 (s; 2H arom.), 6.18-6.01 (m; 1H, NH₂; H/D-exch.), 6.01-5.85 (m; 1H, NH₂; H/D-exch.), 5.17-4.99 (m; 1H, NH₂; H/D-exch.), 4.72-4.60 (m; 2H, CH and NH₂; H/D-exch.: 4.63; ABXY, ³J_{AY} = 1.5 Hz, ³J_{BY} = 11.1 Hz, 1H, CH, H_{ax}), 4.55 (s, br; 1H, CH; H/D-exch.: 4.55; ABXY, ³J_{AX} = 2.0 Hz, ³J_{BX} = 2.0 Hz, 1H, CH, H_{eq}), 2.86 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.33 (ABXY; ²J_{AB} = 14.9 Hz, ³J_{AX} = 2.0 Hz, ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq})- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1144.9 ((L₂Pt₂Cl₃)⁺); 775.3 ((M + H + 2 glycerol)⁺); 683.1 ((M + H + glycerol)⁺), 669.1 ((M + H + DMSO)⁺); 647.1 ((M - Cl + glycerol)⁺); 633.1 ((M - Cl + DMSO)⁺); 591.2 ((M + H)⁺); 555.2 ((M - Cl)⁺).

erythro-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**128**)

From **102**; solvent II; 63%, m.p. 211-216°.- C₁₅H₁₆Cl₄N₂O₂Pt (593.2) Calcd. C 30.4 H 2.72 N 4.7 Found C 30.2 H 3.09 N 4.6.- FT-IR (KBr): $\tilde{\nu}$ = 3417 s, br (OH); 3270 s, 3222 s, 3135 s (NH₂); 2973 w, 2932 w (C-H aliph.); 1603 s, 1574 s (C=C and NH₂)- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.23-6.78 (m; 4H arom.), 6.89 (s; 2H arom.), 6.18-5.98 (m; 1H, NH₂; H/D-exch.), 5.87-5.62 (m; 1H, NH₂; H/D-exch.), 5.29-5.15 (m; 1H, NH₂; H/D-exch.), 5.15-4.98 (m; 1H, CH; H/D-exch.: 5.09; ABXY, ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 10.6 Hz), 4.98-4.77 (m; 1H, NH₂; H/D-exch.), 4.43-4.29 (m; 1H, CH; H/D-exch.: 4.32; ABXY, ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 10.6 Hz), 2.99 (ABXY; ²J_{AB} = 14.5 Hz, ³J_{BX} = ³J_{BY} = 10.6 Hz, 1H, CH₂, H_{ax}, partial overlap with solvent signals), 1.88 (ABXY; ²J_{AB} = 14.5 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq})- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1145.2 ((L₂Pt₂Cl₃)⁺); 683.2 ((M + H + glycerol)⁺); 669.2 ((M + H + DMSO)⁺); 647.3 ((M - Cl + glycerol)⁺); 633.2 ((M - Cl + DMSO)⁺); 591.2 ((M + H)⁺); 555.2 ((M - Cl)⁺).

threo-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**129**)

From **103**; solvent II; 66%, m.p. 225-229°.- C₁₅H₁₆Cl₄N₂O₂Pt x 0.5 tert.-C₄H₁₀O (630.3) Calcd. C 32.4 H 3.36 N 4.4 Found C 32.1 H 3.22 N 4.5.- FT-IR (KBr): $\tilde{\nu}$ = 3395 s, br (OH); 3276 s, 3239 s, 3131 s (NH₂); 3085 w (C-H arom.); 2973 w (C-H aliph.); 1603 s (C=C and NH₂)- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.74-6.82 (m; 4H arom.), 6.84 (s; 2H arom.), 6.18-6.01 (m; 1H, NH₂; H/D-exch.), 6.01-5.84 (m; 1H, NH₂; H/D-exch.), 5.27-5.11 (m; 1H, NH₂; H/D-exch.), 4.71-4.52 (m; 2H, CH and NH₂; H/D-exch.: 4.60; ABXY, ³J_{AY} = 1.5 Hz, ³J_{BY} = 10.1 Hz, 1H, CH, H_{ax}), 4.36 (s, br; 1H, CH; partial overlap with solvent signals after H/D-exch., H_{eq}), 2.93 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.13 (ABXY; ²J_{AB} = 15.0 Hz, ³J_{AX} = 2.0 Hz, ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}), 1.17 (s; 4.5 H, CH₃)- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 775.2 ((M + H + 2 glycerol)⁺), 683.2 ((M + H + glycerol)⁺); 669.2 ((M + H + DMSO)⁺); 647.3 ((M - Cl + glycerol)⁺); 633.3 ((M - Cl + DMSO)⁺); 591.2 ((M + H)⁺); 555.2 ((M - Cl)⁺).

erythro-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**130**)

From **104**; solvent II; 56%, m.p. 212-215°.- C₁₅H₁₆Cl₄N₂O₂Pt (593.2) Calcd. C 30.4 H 2.72 N 4.7 Found C 30.4 H 3.01 N 4.7.- FT-IR (KBr): $\tilde{\nu}$ = 3415 s, br (OH); 3284 s, 3222 s, 3143 s (NH₂); 2963 w, 2915 w (C-H

aliph.); 1611 s, 1601 s, 1570 s (C=C and NH₂).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.14 (s, br; 2H, OH; H/D-exch.), 7.43, 6.83 (AA'BB'; ³J_{AB} = 8.5 Hz, 4H arom.), 6.92 (s; 2H arom.), 6.15-5.97 (m; 1H, NH₂; H/D-exch.), 5.79-5.57 (m; 1H, NH₂; H/D-exch.), 5.20-4.99 (m; 2H, CH and NH₂; H/D-exch.: 5.09; ABXY, ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 10.3 Hz), 4.99-4.79 (m; 1H, NH₂; H/D-exch.), 4.42-4.23 (m; 1H, CH; H/D-exch.: 4.31; ABXY, ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 10.3 Hz), 3.00 (ABXY; ²J_{AB} = 15.5 Hz, ³J_{BX} = ³J_{BY} = 10.3 Hz, 1H, CH₂, H_{ax}, partial overlap with solvent signals), 1.87 (ABXY; ²J_{AB} = 15.5 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1145.6 ((L₂Pt₂Cl₃)⁺); 683.0 ((M + H + glycerol)⁺); 669.0 ((M + H + DMSO)⁺); 647.0 ((M - Cl + glycerol)⁺); 633.0 ((M - Cl + DMSO)⁺); 591.0 ((M + H)⁺); 555.1 ((M - Cl)⁺).

threo-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (131)

From **105**; solvent II; 50%, m.p. 202-205°.- C₁₅H₁₆Cl₄N₂O₂Pt (593.2) Calcd. C 30.4 H 2.72 N 4.7 Found C 30.6 H 2.89 N 4.6.- FT-IR (KBr): $\tilde{\nu}$ = 3413 s, br (OH); 3251 s, 3220 s, 3127 s (NH₂); 2946 w, 2921 w (C-H aliph.); 1603 s, 1574 s (C=C and NH₂).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 8.05, 6.93 (AA'BB'; ³J_{AB} = 8.6 Hz, 4H arom.), 6.85 (s; 2H arom.), 6.02-5.95 (m; 1H, NH₂; H/D-exch.), 5.90-5.80 (m; 1H, NH₂; H/D-exch.), 5.21-5.13 (m; 1H, NH₂; H/D-exch.), 4.71-4.52 (m; 2H, CH and NH₂; H/D-exch.: 4.65; ABXY, ³J_{AY} = 1.5 Hz, ³J_{BY} = 10.9 Hz, 1H, CH, H_{ax}), 4.36 (s, br; 1H, CH; H/D-exch.: 4.37; ABXY, ³J_{AX} = 2.0 Hz, ³J_{BX} = 2.0 Hz, 1H, CH, H_{eq}), 2.98 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.14 (ABXY; ²J_{AB} = 14.2 Hz, ³J_{AX} = 2.0 Hz, ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 775.1 ((M + H + 2 glycerol)⁺); 683.0 ((M + H + glycerol)⁺); 669.0 ((M + H + DMSO)⁺); 647.1 ((M - Cl + glycerol)⁺); 633.1 ((M - Cl + DMSO)⁺); 555.0 ((M - Cl)⁺).

meso-Dichloro-1,3-bis-(2-fluoro-4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (132)

From **106**; solvent II; 20%, m.p. 202-206°.- C₁₅H₁₆Cl₂F₂N₂O₂Pt x H₂O (578.3) Calcd. C 31.2 H 3.14 N 4.9 Found C 31.6 H 3.42 N 4.8.- FT-IR (KBr): $\tilde{\nu}$ = 3432 s, br (OH); 3210 s, 3137 m (NH₂); 2965 w, 2932 w (C-H aliph.); 1628 s (NH₂); 1597 s (C=C).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.22 (s; 2H, OH; H/D-exch.), 7.52 (t; ³J = 8.7 Hz, ⁴J_{HF} = 8.7 Hz, 2H arom.), 6.75-6.59 (m; 4H arom.), 5.60-5.39 (m; 2H, NH₂; H/D-exch.), 5.39-5.22 (m; 2H, NH₂; H/D-exch.), 4.69-4.49 (m; 2H, CH; H/D-exch.: 4.58; ABX₂, ³J_{AX} = 1.0 Hz, ³J_{BX} = 10.7 Hz), 2.78 (ABX₂; ²J_{AB} = 15.1 Hz, ³J_{BX} = 10.7 Hz, 1H, CH₂, H_{ax}), 2.03 (ABX₂; ²J_{AB} = 15.1 Hz, ³J_{AX} = 1.0 Hz, 1H, CH₂, H_{eq}).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1080.8 ((L₂Pt₂Cl₃)⁺); 743.2 ((M + H + 2 glycerol)⁺); 651.0 ((M + H + glycerol)⁺); 637.0 ((M + H + DMSO)⁺); 615.1 ((M - Cl + glycerol)⁺); 601.1 ((M - Cl + DMSO)⁺); 523.1 ((M - Cl)⁺).

rac-Dichloro-1,3-bis-(2-fluoro-4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (133)

From **107**; solvent II; 38%, m.p. 203-206°.- C₁₅H₁₆Cl₂F₂N₂O₂Pt (560.3) Calcd. C 32.2 H 2.88 N 5.0 Found C 32.0 H 2.87 N 4.9.- FT-IR (KBr): $\tilde{\nu}$ = 3432 s, br (OH); 3268 s, 3249 s, 3199 s, 3123 s (NH₂); 3052 w (C-H arom.); 2967 w, 2938 w (C-H aliph.); 1624 s (NH₂); 1593 s (C=C).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.22 (s, br; 2H, OH; H/D-exch.), 8.45 (t; ³J = 8.8 Hz, ⁴J_{HF} = 8.8 Hz, 2H arom.), 6.81-6.57 (m; 4H arom.), 6.83-6.78 (m; 2H arom.), 5.80-5.55 (m; 2H, NH₂; H/D-exch.), 5.55-5.27 (m; 2H, NH₂; H/D-exch.), 4.24 (s, br; 2H, CH; partial overlap with solvent signals after H/D-exch.), 2.29 (A₂X₂, ³J_{AX} = 5.0 Hz, 2H, CH₂).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1181.0 ((L₂Pt₂Cl₃)⁺); 743.2 ((M + H + 2 glycerol)⁺); 651.1 ((M + H + glycerol)⁺); 637.1 ((M + H + DMSO)⁺);

615.2 ((M - Cl + glycerol)⁺); 601.2 ((M - Cl + DMSO)⁺); 569.2 ((M + H)⁺); 523.1 ((M - Cl)⁺).

meso-Dichloro-1,3-bis-(2-chloro-4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (134)

From **108**; solvent II; 45%, m.p. 221-224°.- C₁₅H₁₆Cl₄N₂O₂Pt (593.2) Calcd. C 30.4 H 2.72 N 4.7 Found C 31.0 H 2.86 N 4.6.- FT-IR (KBr): $\tilde{\nu}$ = 3313 s, br (OH); 3268 w, 3231 s, 3201 w, 3123 s (NH₂); 2965 w, 2936 w (C-H aliph.); 1609 s, 1578 s (C=C and NH₂).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.25 (s, br; 2H, OH; H/D-exch.), 7.63 (d; ³J = 8.6 Hz, 2H arom.), 6.94-6.82 (m; 4H arom.), 5.72-5.57 (m, br; 2H, NH₂; H/D-exch.), 5.37-5.26 (m, br; 2H, NH₂; H/D-exch.), 4.74-4.62 (m; 2H, CH; H/D-exch.: 4.72; ABX₂, ³J_{AX} = 1.0 Hz, ³J_{BX} = 12.7 Hz), 2.44 (ABX₂; ²J_{AB} = 15.2 Hz, ³J_{BX} = 12.7 Hz, 1H, CH₂, H_{ax}), 1.98 (ABX₂; ²J_{AB} = 15.2 Hz, ³J_{AX} = 1.0 Hz, 1H, CH₂, H_{eq}).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1145.6 ((L₂Pt₂Cl₃)⁺); 682.9 ((M + H + glycerol)⁺); 669.0 ((M + H + DMSO)⁺); 646.9 ((M - Cl + glycerol)⁺); 632.9 ((M - Cl + DMSO)⁺); 555.0 ((M - Cl)⁺).

rac-Dichloro-1,3-bis-(2-chloro-4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (135)

From **109**; solvent II; 34%, m.p. 216-220°.- C₁₅H₁₆Cl₄N₂O₂Pt x 2 H₂O (629.2) Calcd. C 28.6 H 3.20 N 4.5 Found C 28.2 H 2.90 N 4.3.- FT-IR (KBr): $\tilde{\nu}$ = 3422 s, br (OH); 3249 s, 3203 s, 3121 s (NH₂); 2961 w, 2929 w (C-H aliph.); 1611 s, 1591 m, 1578 s (C=C and NH₂).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 8.74 (d; ³J = 8.5 Hz, 2H arom.), 7.02-6.86 (m; 4H arom.), 5.70-5.60 (m, br; 2H, NH₂; H/D-exch.), 5.47-5.38 (m, br; 2H, NH₂; H/D-exch.), 4.32 (s, br; 2H, CH; partial overlap with solvent signals after H/D-exch.), 2.24 (A₂X₂, ³J_{AX} = 5.0 Hz, 2H, CH₂).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1145.7 ((L₂Pt₂Cl₃)⁺); 775.1 ((M + H + 2 glycerol)⁺); 683.1 ((M + H + glycerol)⁺); 669.2 ((M + H + DMSO)⁺); 647.2 ((M - Cl + glycerol)⁺); 633.1 ((M - Cl + DMSO)⁺); 555.1 ((M - Cl)⁺).

erythro-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(2-fluoro-4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (136)

From **110**; solvent II; 53%, m.p. 206-209°.- C₁₅H₁₅Cl₄FN₂O₂Pt (611.2) Calcd. C 29.5 H 2.47 N 4.6 Found C 29.6 H 2.79 N 4.4.- FT-IR (KBr): $\tilde{\nu}$ = 3422 s, br (OH); 3278 s, 3224 s (NH₂); 2967 w, 2930 w (C-H aliph.); 1626 s, 1603 s (NH₂); 1572 s (C=C).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.24 (s, br; 2H, OH; H/D-exch.), 7.57 (t; ³J = 8.8 Hz, ⁴J_{HF} = 8.8 Hz, 1H arom.), 6.94 (s; 2H arom.), 6.74-6.60 (m; 2H arom.), 6.19-6.02 (m; 1H, NH₂; H/D-exch.), 5.79-5.62 (m; 1H, NH₂; H/D-exch.), 5.47-5.33 (m; 1H, NH₂; H/D-exch.), 5.21-5.02 (m; 1H, CH; H/D-exch.: 5.10; ABXY, ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 12.1 Hz), 5.02-4.82 (m; 1H, NH₂; H/D-exch.), 4.63-4.43 (m; 1H, CH; partial overlap with solvent signals after H/D-exch.), 3.02 (ABXY; ²J_{AB} = 14.3 Hz, ³J_{BX} = ³J_{BY} = 12.1 Hz, 1H, CH₂, H_{ax}, partial overlap with solvent signals), 1.91 (ABXY; ²J_{AB} = 14.3 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1181.4 ((L₂Pt₂Cl₃)⁺); 701.2 ((M + H + glycerol)⁺); 687.1 ((M + H + DMSO)⁺); 665.2 ((M - Cl + glycerol)⁺); 651.3 ((M - Cl + DMSO)⁺); 573.2 ((M - Cl)⁺).

threo-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(2-fluoro-4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (137)

From **111**; solvent II; 65%, m.p. 196-199°.- C₁₅H₁₅Cl₄FN₂O₂Pt (611.2) Calcd. C 29.5 H 2.48 N 4.6 Found C 29.8 H 3.02 N 4.4.- FT-IR (KBr): $\tilde{\nu}$ = 3378 s, br (OH); 3276 s, 3129 m (NH₂); 3010 w (C-H arom.); 2963 w, 2927 w (C-H aliph.); 1626 s, 1603 s (NH₂); 1572 s (C=C).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 9.29 (t; ³J = 8.8 Hz, ⁴J_{HF} = 8.8 Hz, 1H arom.), 6.93-6.63 (m; 2H arom.), 6.86 (s; 2H arom.), 6.27-6.08 (m;

1H, NH₂), 6.08-5.90 (m; 1H, NH₂), 5.28-5.03 (m; 1H, NH₂), 4.78-4.57 (m; 2H, CH, H_{ax} and NH₂), 4.53 (s, br; 1H, CH, H_{eq}), 3.02-2.90 (m; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.01 (ABXY; ²J_{AB} = 14.9 Hz, ⁴J_{AX} = 2.0 Hz, ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}). PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1181.5 ((L₂Pt₂Cl₃)⁺); 793.3 ((M + H + 2 glycerol)⁺); 701.1 ((M + H + glycerol)⁺); 687.3 ((M + H + DMSO)⁺); 665.3 ((M - Cl + glycerol)⁺); 651.2 ((M - Cl + DMSO)⁺); 609.1 ((M + H)⁺); 573.1 ((M - Cl)⁺).

erythro-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(2-chloro-4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (138)

From **112**; solvent II; 71%, m.p. 202-205°. C₁₅H₁₅Cl₅N₂O₂Pt x H₂O (645.7) Calcd. C 27.9 H 2.65 N 4.3 Found C 28.0 H 2.82 N 4.1. FT-IR (KBr): $\tilde{\nu}$ = 3422 s, br (OH); 3284 s, 3224 s, 3139 s (NH₂); 2929 w (C-H aliph.), 1607 s, 1570 s (C=C and NH₂). ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.29 (s, br; 2H, OH; H/D-exch.), 7.66 (d; ³J = 8.5 Hz, 1H arom.), 7.01-6.86 (m; 2H arom.), 6.93 (s; 2H arom.), 6.23-6.06 (m; 1H, NH₂; H/D-exch.), 5.90-5.71 (m; 1H, NH₂; H/D-exch.), 5.50-5.34 (m; 1H, NH₂; H/D-exch.), 5.31-5.01 (m; 1H, CH; H/D-exch.: 5.11; ABXY; ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 11.3 Hz), 5.01-4.77 (m; 1H, NH₂; H/D-exch.), 4.77-4.52 (m; 1H, CH; H/D-exch.: 4.63; ABXY; ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 11.3 Hz), 2.93 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 1.92 (ABXY; ²J_{AB} = 14.7 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}). PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1213.3 ((L₂Pt₂Cl₃)⁺); 703.1 ((M + H + DMSO)⁺); 681.1 ((M - Cl + glycerol)⁺); 667.1 ((M - Cl + DMSO)⁺); 589.2 ((M - Cl)⁺).

threo-Dichloro-1-(2,6-dichloro-4-hydroxyphenyl)-3-(2-chloro-4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (139)

From **113**; solvent II; 68%, m.p. 216-220°. C₁₅H₁₅Cl₅N₂O₂Pt (627.6) Calcd. C 28.7 H 2.41 N 4.5 Found C 29.3 H 2.91 N 4.4. FT-IR (KBr): $\tilde{\nu}$ = 3340 s, br (OH); 3274 s, 3237 s, 3193 s, 3131 s (NH₂); 2932 w (C-H aliph.); 1609 s, 1574 s (C=C and NH₂). ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.30 (s, br; 2H, OH; H/D-exch.), 9.56 (d; ³J = 8.6 Hz, 1H arom.), 7.10-6.91 (m; 2H arom.), 6.87 (s; 2H arom.), 6.34-6.11 (m; 1H, NH₂), 6.11-5.97 (m; 1H, NH₂), 5.34-5.07 (m; 1H, NH₂), 4.82-4.50 (m; 3H, 2 CH and 1 NH₂), 2.97-2.86 (m; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.09 (ABXY; ²J_{AB} = 13.2 Hz, ³J_{AX} = 2.0 Hz, ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}). PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 1213.6 ((L₂Pt₂Cl₃)⁺); 717.1 ((M + H + glycerol)⁺); 703.0 ((M + H + DMSO)⁺); 681.2 ((M - Cl + glycerol)⁺); 667.2 ((M - Cl + DMSO)⁺); 625.2 ((M + H)⁺); 589.2 ((M - Cl)⁺).

Diiodo-Pt(II) complexes

The title complexes were prepared from the 1,3-diphenylpropane-1,3-diamine-dihydrobromides (0.5 mmoles), liberating the corresponding bases as described for the corresponding dichloro-Pt(II) complexes with the solvent indicated there. To the solution of the base (if necessary tert-butanol is added, see above) of pH 6.5 K₂PtI₄-solution (prepared from 208 mg (0.5 mmole) K₂PtCl₄ and 0.750 g KI in 1.25 ml of water by stirring for 30 min in the dark at room temp.) was added drop by drop. The mixture was stirred at room temp. adjusting the pH-value to 6.5 until it does not change anymore. Then the precipitated analytically pure complex is filtered off by suction, washed with 2N HCl and water and dried at 100° for several days over P₄O₁₀ *in vacuo*. All complexes are yellow to ochre coloured powders.

meso-Diiodo-1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino Pt(II) (140)

From **88**; 51%, m.p. 224-228°. C₁₅H₁₈I₂N₂O₂Pt (707.2) Calcd. C 25.5 H 2.57 N 4.0 Found C 25.4 H 2.76 N 4.0. FT-IR (KBr): $\tilde{\nu}$ = 3432 s, br (OH); 3257 s, 3187 s, 3121 s (NH₂); 3052 w (C-H arom.); 2925 w (C-H aliph.); 1603 s, 1591 s (C=C and NH₂). ¹H-NMR ([D₇]DMF): δ (ppm/250

MHz) = 9.72 (s; 2H, OH; H/D-exch.), 7.25-6.80 (m; 8H arom.), 5.65-5.49 (m, br; 2H, NH₂), 4.89-4.64 (m, br; 2H, NH₂), 4.53-4.36 (m; 2H, CH), 2.55 (ABX₂; ²J_{AB} = 14.2 Hz, ³J_{BX} = 11.4 Hz, 1H, CH₂, H_{ax}), 2.13 (ABX₂; ²J_{AB} = 14.2 Hz, ³J_{AX} = 1.0 Hz, 1H, CH₂, H_{eq}). PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 785.8 ((M + H + DMSO)⁺); 749.0 ((M - I + DMSO + glycerol)⁺); 671.0 ((M - I + glycerol)⁺); 657.0 ((M - I + DMSO)⁺); 579.0 ((M - I)⁺).

rac-Diiodo-1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (141)

From **89**; 93%, m.p. 196-198°. C₁₅H₁₈I₂N₂O₂Pt x H₂O (725.2) Calcd. C 24.8 H 2.78 N 3.9 Found C 24.8 H 3.10 N 3.7. FT-IR (KBr): $\tilde{\nu}$ = 3395 m, br (OH); 3264 s, 3247 s, 3181 s, 3121 s (NH₂); 3052 w (C-H arom.); 2969 w, 2932 w (C-H aliph.); 1601 s (C=C and NH₂). ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 9.72 (s, br; 2H, OH; H/D-exch.), 7.27-6.77 (m; 8H arom.), 5.42-5.29 (m, br; 2H, NH₂; H/D-exch.), 5.28-5.19 (m, br; 2H, NH₂; H/D-exch.), 4.17 (s, br; 2H, CH; H/D-exch.: 4.16; A₂X₂, ³J_{AX} = 5.0 Hz), 2.47 (A₂X₂; ³J_{AX} = 5.0 Hz, 2H, CH₂). PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 785.8 ((M + H + DMSO)⁺); 749.0 ((M - I + DMSO + glycerol)⁺); 671.0 ((M - I + glycerol)⁺); 657.0 ((M - I + DMSO)⁺); 579.1 ((M - I)⁺).

erythro-Diiodo-1-(2-fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (142)

From **94**; 71%, m.p. 188-191°. C₁₅H₁₇FI₂N₂O₂Pt (725.2) Calcd. C 24.8 H 2.36 N 3.9 Found C 24.5 H 2.63 N 3.7. FT-IR (KBr): $\tilde{\nu}$ = 3413 s, br (OH); 3257 s, 3197 s, 3125 s (NH₂); 2959 w, 2927 w (C-H aliph.); 1626 s (NH₂); 1597 s (C=C). ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.24 (s; 1H, OH; H/D-exch.), 9.71 (s; 1H, OH; H/D-exch.), 7.49 (t; ³J = 8.9 Hz, ⁴J_{HF} = 8.9 Hz, 1H arom.), 7.42, 6.85 (AA'BB'; ³J_{AB} = 8.5 Hz, 4H arom.), 6.73-6.61 (m; 2H arom.), 5.70-5.49 (m; 1H, NH₂; H/D-exch.), 5.49-5.29 (m; 1H, NH₂; H/D-exch.), 5.01-4.87 (m; 1H, NH₂; H/D-exch.), 4.75-4.52 (m; 2H, 1 CH and 1 NH₂; H/D-exch.: 4.63; ABXY; ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 10.5 Hz), 4.52-4.33 (m; 1H, CH, overlap with solvent signals), 2.95 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.11 (ABXY; ²J_{AB} = 13.8 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}). PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 803.1 ((M + H + DMSO)⁺); 767.2 ((M - I + DMSO + glycerol)⁺); 689.3 ((M - I + glycerol)⁺); 675.2 ((M - I + DMSO)⁺); 597.3 ((M - I)⁺).

threo-Diiodo-1-(2-fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (143)

From **95**; 55%, m.p. 196-198°. C₁₅H₁₇FI₂N₂O₄Pt (725.2) Calcd. C 24.8 H 2.36 N 3.9 Found C 24.6 H 2.59 N 3.4. FT-IR (KBr): $\tilde{\nu}$ = 3405 s, br (OH); 3270 s, 3249 s, 3193 s, 3133 s (NH₂); 2936 w, 2903 w (C-H aliph.); 1626 s (NH₂); 1593 s (C=C). ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.22 (s; 1H, OH; H/D-exch.), 9.69 (s; 1H, OH; H/D-exch.), 8.24 (t; ³J = 8.8 Hz, ⁴J_{HF} = 8.8 Hz, 1H arom.), 7.69, 6.86 (AA'BB'; ³J_{AB} = 8.5 Hz, 4H arom.), 6.79-6.56 (m; 2H arom.), 5.27 (s, br; 4H, NH₂; H/D-exch.), 4.41 (s, br; 1H, CH; H/D-exch.: 4.37; A₂XY, ³J_{AX} = ³J_{AY} = 5.0 Hz, CH₂), 4.24 (s, br; 1H, CH; H/D-exch.: 4.28; A₂XY, ³J_{AX} = ³J_{AY} = 5.0 Hz), 2.43 (A₂XY; ³J_{AX} = ³J_{AY} = 5.0 Hz). PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): m/z = 803.1 ((M + H + DMSO)⁺); 767.2 ((M - I + DMSO + glycerol)⁺); 689.2 ((M - I + glycerol)⁺); 675.2 ((M - I + DMSO)⁺); 597.2 ((M - I)⁺).

erythro-Diiodo-1-(2-chloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (144)

From **96**; 67%, m.p. 190-192°. C₁₅H₁₇ClI₂N₂O₂Pt x 2 H₂O (777.7) Calcd. C 23.2 H 2.72 N 3.6 Found C 22.9 H 2.46 N 3.5. FT-IR (KBr): $\tilde{\nu}$ = 3424 s, br (OH); 3257 s, 3195 s, 3123 s (NH₂); 2963 w, 2929 w (C-H aliph.); 1611 s, 1578 s (C=C and NH₂). ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.27 (s; 1H, OH; H/D-exch.), 9.72 (s; 1H, OH; H/D-exch.), 7.58

(d; $^3J = 8.6$ Hz, 1H arom.), 7.44, 6.86 (AA'BB'; $^3J_{AB} = 8.5$ Hz, 4H arom.), 7.02-6.78 (m; 2H arom.), 5.73-5.39 (m; 2H, NH₂), 4.98-4.70 (m; 1H, NH₂), 4.70-4.59 (m; 2H, 1 CH and 1 NH₂), 4.59-4.40 (m; 1H, CH), 2.63 ($^2J_{AB} = 13.4$ Hz, $^3J_{BX} = ^3J_{BY} = 11.2$ Hz, 1H, CH₂, H_{ax}, partial overlap with solvent signals), 2.14 (ABXY; $^2J_{AB} = 15.0$ Hz, $^3J_{AX} = ^3J_{AY} = 1.5$ Hz, 1H, CH₂, H_{eq}).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): $m/z = 819.6$ ((M + H + DMSO)⁺); 782.9 ((M - I + DMSO + glycerol)⁺); 704.9 ((M - I + glycerol)⁺); 690.9 ((M - I + DMSO)⁺); 613.0 ((M - I)⁺).

threo-Diiodo-1-(2-chloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**145**)

From **97**; 56%, m.p. 191-193°. - C₁₅H₁₇ClI₂N₂O₂Pt (741.7) Calcd. C 24.3 H 2.31 N 3.8 Found C 24.3 H 2.45 N 3.7.- FT-IR (KBr): $\tilde{\nu} = 3409$ s, br (OH), 3230 s, 3185 s, 3121 s (NH₂); 2909 w (C-H aliph.); 1611 s, 1584 s (C=C and NH₂).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.23 (s; 1H, OH; H/D-exch.), 9.69 (s; 1H, OH; H/D-exch.), 8.30 (d; $^3J = 8.4$ Hz, 1H arom.), 7.78 (d, part of an AA'BB'-system; $^3J_{AB} = 8.6$ Hz, 2H arom.), 6.94-6.80 (m; 4H arom.), 5.55-5.36 (m; 2H, NH₂), 5.36-5.07 (m; 2H, NH₂), 4.46 (s, br; 1H, CH), 4.29 (s, br; 1H, CH), 2.43 (A₂XY; $^3J_{AX} = ^3J_{AY} = 5.0$ Hz, CH₂).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): $m/z = 819.7$ ((M + H + DMSO)⁺); 783.0 ((M - I + DMSO + glycerol)⁺); 705.0 ((M - I + glycerol)⁺); 690.9 ((M - I + DMSO)⁺); 613.0 ((M - I)⁺).

erythro-Diiodo-1-(2,6-dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**146**)

From **102**; 81%, m.p. 185-187°. - C₁₅H₁₆Cl₂I₂N₂O₂Pt x 2 H₂O (812.1) Calcd. C 22.2 H 2.48 N 3.4 Found C 21.9 H 2.29 N 3.4.- FT-IR (KBr): $\tilde{\nu} = 3424$ s, br (OH); 3272 s, 3199 s (NH₂); 2963 w, 2925 w (C-H aliph.); 1605 s, 1570 s (C=C and NH₂).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.81 (s; 1H, OH; H/D-exch.), 9.75 (s; 1H, OH; H/D-exch.), 7.26-6.80 (m; 4H arom.), 6.93 (s; 2H arom.), 6.18-5.98 (m; 1H, NH₂; H/D-exch.), 5.84-5.78 (m; 2H, NH₂), 5.26-4.99 (m; 2H, 1 CH and 1 NH₂), 4.97-4.85 (m; 1H, NH₂), 4.50-4.40 (m; 1H, CH), 3.13 (ABXY; $^2J_{AB} = 15.3$ Hz, $^3J_{BX} = ^3J_{BY} = 11.2$ Hz, 1H, CH₂, H_{ax}), 2.03 (ABXY; $^2J_{AB} = 15.3$ Hz, $^3J_{AX} = ^3J_{AY} = 1.5$ Hz, 1H, CH₂, H_{eq}).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): $m/z = 853.1$ ((M + H + DMSO)⁺); 817.1 ((M - I + DMSO + glycerol)⁺); 739.1 ((M - I + glycerol)⁺); 725.1 ((M - I + DMSO)⁺); 647.2 ((M - I)⁺).

threo-Diiodo-1-(2,6-dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**147**)

From **103**; 85%, m.p. 203-205°. - C₁₅H₁₆Cl₂I₂N₂O₂Pt (776.1) Calcd. C 23.2 H 2.08 N 3.6 Found C 23.7 H 2.48 N 3.6.- FT-IR (KBr): $\tilde{\nu} = 3395$ s, br (OH); 3272 s, 3222 s, 3193 m, 3135 s (NH₂); 2969 w (C-H aliph.); 1603 s, 1568 s (C=C and NH₂).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.81 (s; 1H, OH; H/D-exch.), 9.74 (s; 1H, OH; H/D-exch.), 7.60-6.82 (m; 4H arom.), 6.88 (s; 2H arom.), 5.88-5.56 (m; 2H, NH₂), 5.30-5.12 (m; 1H, NH₂), 4.89-4.62 (m; 2H, 1 CH and 1 NH₂), 4.58 (s, br; 1H, CH), 2.96 (ABXY; 1H, CH₂, H_{ax}, overlap by solvent signals), 2.23 (ABXY; $^2J_{AB} = 14.8$ Hz, $^3J_{AX} = 2.0$ Hz, $^3J_{AY} = 1.5$ Hz, 1H, CH₂, H_{eq}).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): $m/z = 853.0$ ((M + H + DMSO)⁺); 817.1 ((M - I + DMSO + glycerol)⁺); 739.1 ((M - I + glycerol)⁺); 725.0 ((M - I + DMSO)⁺); 647.2 ((M - I)⁺).

erythro-Diiodo-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**148**)

From **104**; 70%, m.p. 183-185°. - C₁₅H₁₆Cl₂I₂N₂O₂Pt x H₂O (794.1) Calcd. C 22.7 H 2.28 N 3.5 Found C 22.6 H 2.36 N 3.5.- FT-IR (KBr): $\tilde{\nu} = 3424$ s, br (OH); 3262 s, 3216 m (NH₂); 2967 w, 2929 w (C-H aliph.); 1605 s, 1570 s (C=C and NH₂).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.82 (s; 1H, OH; H/D-exch.), 9.74 (s; 1H, OH; H/D-exch.), 7.47, 6.86 (AA'BB'; $^3J_{AB} = 8.5$ Hz, 4H arom.), 6.94 (s; 2H arom.), 5.90-5.77 (m;

1H, NH₂), 5.77-5.60 (m; 1H, NH₂), 5.29-4.75 (m; 3H, 1 CH and 2 NH₂), 4.49-4.36 (m; 1H, CH), 3.23 (ABXY; $^2J_{AB} = 15.4$ Hz, $^3J_{BX} = ^3J_{BY} = 11.5$ Hz, 1H, CH₂, H_{ax}), 1.99 (ABXY; $^2J_{AB} = 15.4$ Hz, $^3J_{AX} = ^3J_{AY} = 1.5$ Hz, 1H, CH₂, H_{eq}).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): $m/z = 852.8$ ((M + H + DMSO)⁺); 816.8 ((M - I + DMSO + glycerol)⁺); 738.8 ((M - I + glycerol)⁺); 724.8 ((M - I + DMSO)⁺); 646.9 ((M - I)⁺).

threo-Diiodo-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**149**)

From **105**; 76%, m.p. 172-174°. - C₁₅H₁₆Cl₂I₂N₂O₂Pt x 2 H₂O (812.1) Calcd. C 22.2 H 2.48 N 3.4 Found C 21.9 H 2.26 N 3.1.- FT-IR (KBr): $\tilde{\nu} = 3405$ s, br (OH), 3247 s, 3191 s, 3129 m (NH₂); 2936 w (C-H aliph.); 1605 s, 1570 s (C=C and NH₂).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 10.74 (s; 1H, OH; H/D-exch.), 9.67 (s; 1H, OH; H/D-exch.), 7.94, 6.91 (AA'BB'; $^3J_{AB} = 8.6$ Hz, 4H arom.), 6.88 (s, 2H arom.), 5.87-5.51 (m; 2H, NH₂), 5.28-5.10 (m; 1H, NH₂), 4.98-4.65 (m; 2H, 1 CH and 1 NH₂), 4.57 (s, br; 1H, CH), 2.95 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.23 (ABXY; $^2J_{AB} = 13.0$ Hz, $^3J_{AX} = 2.0$ Hz, $^3J_{AY} = 1.5$ Hz, 1H, CH₂, H_{eq}).- PI-FAB-MS (glycerol/DMSO/¹⁹⁴Pt): $m/z = 852.8$ ((M + H + DMSO)⁺); 816.8 ((M - I + DMSO + glycerol)⁺); 738.8 ((M - I + glycerol)⁺); 724.8 ((M - I + DMSO)⁺); 646.9 ((M - I)⁺).

meso- and rac-Diiodo-1,3-bis-(3,4-dihydroxyphenyl)propane-1,3-diamino-Pt(II) (**150** and **151**)¹⁾

Diaqua/sulfato-1,3-diphenylpropane-1,3-diamino-Pt(II) complexes

Under light protection a suspension of 0.5 mmoles of the pertinent diiodo-1,3-diphenylpropane-1,3-diamino-Pt(II) complex and 148 mg (0.475 mmole) of Ag₂SO₄ in 20 ml of water was stirred for several days, until the reaction for Ag⁺ with 20% NaOH in the supernatant is negative. Then AgI was separated by millipor-filtration and the filtrate was freeze-dried. The complexes were obtained as colourless powders. Melting points cannot be determined.

meso-Diaqua/sulfato-1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**152**)

From **140**; 54%. - C₁₅H₂₂N₂O₈PtS x 3 H₂O (638.6) Calcd. C 28.2 H 4.42 N 4.4 Found C 28.1 H 4.32 N 4.4.- FT-IR (KBr): $\tilde{\nu} = 3407$ s, br (OH and H₂O); 3214 s, 3114 m (NH₂); 2967 w (C-H aliph.); 1603 s, 1593 s (C=C and NH₂); 1217 s, 1163 s, 1119 s, 1030 m, 874 w 592 m (SO₄²⁻).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.20-6.70 (m; 8H arom.), 4.33 (ABX₂; $^3J_{AX} = 1.0$ Hz, $^3J_{BX} = 11.5$ Hz, 2H, CH), 2.50 (ABX₂; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.08 (ABX₂; $^2J_{AB} = 15.3$ Hz, $^3J_{AX} = 1.0$ Hz, 1H, CH₂, H_{eq}).

rac-Diaqua/sulfato-1,3-bis-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**153**)

From **141**; 59%. - C₁₅H₂₂N₂O₈PtS x 2 H₂O (620.5) Calcd. C 29.0 H 4.22 N 4.5 Found C 28.8 H 3.62 N 4.8.- FT-IR (KBr): $\tilde{\nu} = 3407$ s, br (OH and H₂O); 3214 s, 3112 m (NH₂); 2965 w, 1942 w (C-H aliph.); 1591 s (C=C and NH₂); 1163 s, 1121 s, 1030 m, 955 w, 592 m (SO₄²⁻).- ¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.41-6.76 (m; 6H arom.), 3.94 (A₂X₂, $^3J_{AX} = 5.0$ Hz, 2H, CH), 2.50 (A₂X₂; $^3J_{AX} = 5.0$ Hz, 2H, CH₂).

rac-Diaqua/sulfato-1,3-bis-(3,4-dihydroxyphenyl)propane-1,3-diamino-Pt(II) (**154**)

From **151**; 62%. - C₁₅H₂₂N₂O₁₀PtS x 0.5 H₂O (626.5) Calcd. C 28.8 H 3.70 N 4.5 Found C 28.9 H 4.06 N 4.7.- FT-IR (KBr): $\tilde{\nu} = 3400$ s, br (OH and H₂O); 3203 s, 3125 m (NH₂); 3032 w (C-H arom.); 2961 w (C-H aliph.); 1609 s (C=C and NH₂); 1194 s, 1115 s, 1026 m, 945 w, 590 m

(SO₄²⁻)-¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.49-6.78 (m; 6H arom.), 3.83 (A₂X₂; 2H, CH, overlap with solvent signals), 2.49 (A₂X₂; ³J_{AX} = 5.0 Hz, 2H, CH₂).

erythro-Diaqua/sulfato-1-(2-fluoro-4-hydroxyphenyl)-4-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**155**)

From **142**; 72%.- C₁₅H₂₁FN₂O₈PtS x 2 H₂O (639.5) Calcd. C 28.2 H 3.94 N 4.4 Found C 28.2 H 3.99 N 4.6.- FT-IR (KBr): $\tilde{\nu}$ = 3422 s, br (OH and H₂O); 3206 s, 3125 m (NH₂); 2963 w, 2929 w (C-H aliph.); 1628 s (NH₂); 1597 s (C=C); 1223 s, 1178 s, 1032 m, 968 m, 617 m, 592 m (SO₄²⁻)-¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.55 (t; ³J = 8.5 Hz, ⁴J_{HF} = 8.5 Hz, 1H arom.), 7.48-6.46 (m; 6H arom.), 4.55 (ABXY; ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 11.3 Hz, 1H, CH), 4.25 (ABXY; 1H, CH, overlap with solvent signals), 2.54 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.00 (ABXY; ²J_{AB} = 15.3 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}).

threo-Diaqua/sulfato-1-(2-fluoro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**156**)

From **143**; 84%.- C₁₅H₂₁FN₂O₈PtS (603.5) Calcd. C 29.9 H 3.51 N 4.6 Found C 29.8 H 3.37 N 4.7.- FT-IR (KBr): $\tilde{\nu}$ = 3374 s, br (OH and H₂O); 3218 s, 3129 m (NH₂); 2967 w (C-H aliph.); 1628 s, 1616 s (NH₂); 1597 s (C=C); 1209 m, 1182 s, 1024 s, 588 m (SO₄²⁻)-¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 8.30 (t; 1H arom., overlap with solvent signals), 7.63-6.55 (m; 6H arom.), 4.26 (A₂XY; ³J_{AX} = ³J_{AY} = 5.0 Hz, 1H, CH), 3.92 (A₂XY; ³J_{AX} = ³J_{AY} = 5.0 Hz, 1H, CH), 2.40 (A₂XY; ³J_{AX} = ³J_{AY} = 5.0 Hz, 2H, CH₂).

erythro-Diaqua/sulfato-1-(2-chloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**157**)

From **144**; 48%.- C₁₅H₂₁ClN₂O₈PtS x 4 H₂O (692.0) Calcd. C 26.0 H 4.22 N 4.0 Found C 25.6 H 3.62 N 4.0.- FT-IR (KBr): $\tilde{\nu}$ = 3407 s, br (OH and H₂O); 3210 s, 3116 m (NH₂); 2970 w (C-H aliph.); 1613 s, 1582 s (C=C and NH₂); 1178 s, 1115 m, 1030 s, 947 w, 592 m (SO₄²⁻)-¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 8.08-6.78 (m; 7H arom.), 4.68 (ABXY; ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 12.7 Hz, 1H, CH), 4.34 (ABXY; ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 12.7 Hz, 1H, CH); 2.50 (ABXY; 1H, CH₂, H_{ax}, overlap by solvent signals), 1.91 (ABXY; ²J_{AB} = 15.3 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}).

threo-Diaqua/sulfato-1-(2-chloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**158**)

From **145**; 55%.- C₁₅H₂₁ClN₂O₈PtS x 0.5 H₂O (629.0) Calcd. C 28.6 H 3.53 N 4.5 Found C 28.4 H 3.16 N 4.3.- FT-IR (KBr): $\tilde{\nu}$ = 3424 s, br (OH and H₂O); 3260 s, 3120 m (NH₂); 2969 w (C-H aliph.); 1611 s, 1578 m (C=C and NH₂); 1209 s, 1113 s, 1036 m, 953 w, 592 m (SO₄²⁻)-¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.98-6.83 (m; 4H arom.), 4.28 (A₂XY; ³J_{AX} = ³J_{AY} = 5.0 Hz, 1H, CH), 4.00 (A₂XY; overlap with solvent signals), 2.46 (A₂XY; ³J_{AX} = ³J_{AY} = 5.0 Hz, 2H, CH₂).

erythro-Diaqua/sulfato-1-(2,6-dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**159**)

From **146**; 32%.- C₁₅H₂₀Cl₂N₂O₈PtS x 1.5 H₂O (681.4) Calcd. C 26.4 H 3.40 N 4.1 Found C 26.6 H 3.95 N 4.1.- FT-IR (KBr): $\tilde{\nu}$ = 3424 s, br (OH

and H₂O); 3266 s (NH₂); 2969 w, 2932 w (C-H aliph.); 1605 s, 1570 s (C=C and NH₂); 1205 s, 1070 m, 955 w, 592 m (SO₄²⁻)-¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.23-6.78 (m; 4H arom.), 6.92 (s; 2H arom.), 5.09 (ABXY; ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 10.6 Hz, 1H, CH), 4.00 (ABXY; 1H, CH, overlap with solvent signals), 2.99 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 1.91 (ABXY; ²J_{AB} = 14.3 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}).

threo-Diaqua/sulfato-1-(2,6-dichloro-4-hydroxyphenyl)-3-(3-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**160**)

From **147**; 37%.- C₁₅H₂₀Cl₂N₂O₈PtS x H₂O (672.4) Calcd. C 26.8 H 3.28 N 4.2 Found C 26.6 H 3.59 N 4.3.- FT-IR (KBr): $\tilde{\nu}$ = 3422 s, br (OH and H₂O); 3224 s (NH₂); 2954 w (C-H aliph.); 1605 s, 1572 s (C=C and NH₂); 1221 s, 1192 s, 1119 m, 1030 m, 953 w, 592 m (SO₄²⁻)-¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.76-6.85 (m; 4H arom.), 6.89 (s; 2H arom.), 4.75 (ABXY; ³J_{AY} = 1.5 Hz, ³J_{BY} = 11.1 Hz, 1H, CH, H_{ax}), 4.21 (ABXY; 1H, CH, H_{eq}, overlap with solvent signals), 2.90 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.15 (ABXY; ²J_{AB} = 15.3 Hz, ³J_{AX} = 2.0 Hz, ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}).

erythro-Diaqua/sulfato-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**161**)

From **148**, 36%.- C₁₅H₂₀Cl₂N₂O₈PtS x 2 H₂O (690.4) Calcd. C 26.1 H 3.50 N 4.1 Found C 26.4 H 3.85 N 4.4.- FT-IR (KBr): $\tilde{\nu}$ = 3424 s, br (OH and H₂O); 3268 s (NH₂); 2930 w (C-H aliph.); 1607 s, 1572 s (C=C and NH₂); 1177 s, 1028 m, 955 w, 594 m (SO₄²⁻)-¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 7.42, 6.83 (AA'BB'; ³J_{AB} = 8.5 Hz, 4H arom.), 6.93 (s; 2H arom.), 5.16 (ABXY; ³J_{AX} = ³J_{AY} = 1.5 Hz, ³J_{BX} = ³J_{BY} = 12.4 Hz, 1H, CH), 4.42 (ABXY; 1H, CH, overlap with solvent signals), 2.95 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 1.89 (ABXY; ²J_{AB} = 14.9 Hz, ³J_{AX} = ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}).

threo-Diaqua/sulfato-1-(2,6-dichloro-4-hydroxyphenyl)-3-(4-hydroxyphenyl)propane-1,3-diamino-Pt(II) (**162**)

From **149**; 44%.- C₁₅H₂₀Cl₂N₂O₈PtS x 4 H₂O (726.5) Calcd. C 24.8 H 3.89 N 3.9 Found C 24.6 H 3.34 N 3.9.- FT-IR (KBr): $\tilde{\nu}$ = 3415 s, br (OH and H₂O); 3266 s, 3228 s (NH₂); 1605 s, 1572 s (C=C and NH₂); 1209 s, 1119 m, 1028 m, 955 w, 592 m (SO₄²⁻)-¹H-NMR ([D₇]DMF): δ (ppm/250 MHz) = 8.05-6.82 (m; 6H arom.), 4.69 (ABXY; ³J_{AY} = 1.5 Hz, ³J_{BY} = 11.4 Hz, 1H, CH, H_{ax}), 4.29 (ABXY; 1H, CH, H_{eq}, overlap with solvent signals), 2.95 (ABXY; 1H, CH₂, H_{ax}, overlap with solvent signals), 2.19 (ABXY; ²J_{AB} = 14.8 Hz, ³J_{AX} = 2.0 Hz, ³J_{AY} = 1.5 Hz, 1H, CH₂, H_{eq}).

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